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Integration of CO_2 capture and storage based on pH–swing mineral carbonation using recyclable ammonium salts

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Abstract

The integration of CO_2 capture and storage process based on mineral carbonation using recyclable ammonium salts is a new approach to capture carbon dioxide and convert it into mineral carbonates. This process avoids stripping CO_2 as pure gas from absorbents and compression of CO_2, and therefore reduces energy consumption. The additives used in this process are recyclable ammonium salts, the NH_4HSO_4 and NH_4HCO_3. The results from extraction experiments show that NH_4HSO_4 was able to extract 100% of magnesium from serpentine at 100 °C after 3 hours. And the precipitation of hydromagnesite using NH_4HCO_3 solution is much more effective than using CO_2, where the highest magnesium carbonation achieved 96%. Based on the experimental results, this process shows that the process has the potential to be cost-effective.

Keywords: Integrated capture and storage, mineral carbonation, recycable, ammonium salts, serpentine

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1. Introduction

The integrated CO_2 capture and storage process based on mineral carbonation is a new approach to capture carbon dioxide from power plant flue gas and convert it into mineral carbonates. The carbonates are benign and geologically stable and their CO_2 content is as high as 40%. This process differs from the CO_2 geo-sequestration process, as it avoids the need to strip CO_2 from flue gas scrubbing media and compression for mostly long-distance transport by pipeline. It should be noted that stripping and compression consume at least 25% of the energy released from power plant [1].

Mineral sequestration is a promising strategy to permanently and safely store anthropogenic generated CO_2 in solid Mg- and Ca- carbonates. Advantages of mineral carbonation include vast storage capacity, permanent storage, less leakage risk and the fact that mineralization is an exothermal reaction. However, mineral sequestration also faces many problems such as low efficiency, slow kinetics, and energy intensive pre-treatment processes [2]. Right now, the development of aqueous indirect CO_2 mineral sequestration overcomes the barriers of low efficiency and high energy pre-treatment, but it is still limited by the slow reaction rate of mineral dissolution and unrecyclable use of additives. Generally, large amounts of acid and base are required for the mineral dissolution and carbonate reactions. The cost for make-up chemicals alone (600–1600 US$/t CO_2) is much more than the price for CO_2 emission allowances (30-40 US$/t CO_2) [1]. Thus, recycling of all chemicals involved is important in indirect processes for economic reasons.

In order to overcome the limitations discussed above, a new process of integrated capture and storage based on mineral carbonation using recyclable ammonium salts has been developed and is described here (Figure 1). Firstly, ammonia is used to capture CO_2 from power plant's flue gas and produce ammonium bicarbonate (NH_4HCO_3) in the capture step. Secondly, ammonium bisulphate (NH_4HSO_4) is used to extract Mg ions from serpentine at mild heating conditions in mineral dissolution step. Thirdly, the Mg-rich solution produced from mineral dissolution is regulated to neutral pH by adding ammonia water; the impurities in the leaching solution are then removed by adding ammonia water. After that, the solution reacts with the intermediate product (ammonium bicarbonate (NH_4HCO_3)) from the CO_2 capture step to precipitate carbonates at mild temperature. With the precipitation of hydromagnesite, the final solution mainly contains ammonium sulphate. Finally, the ammonium sulphate could be collected by evaporation and subsequently heated up to regenerate ammonia which will go back to the capture step and ammonium bisulphate which is reused in the mineral dissolution.

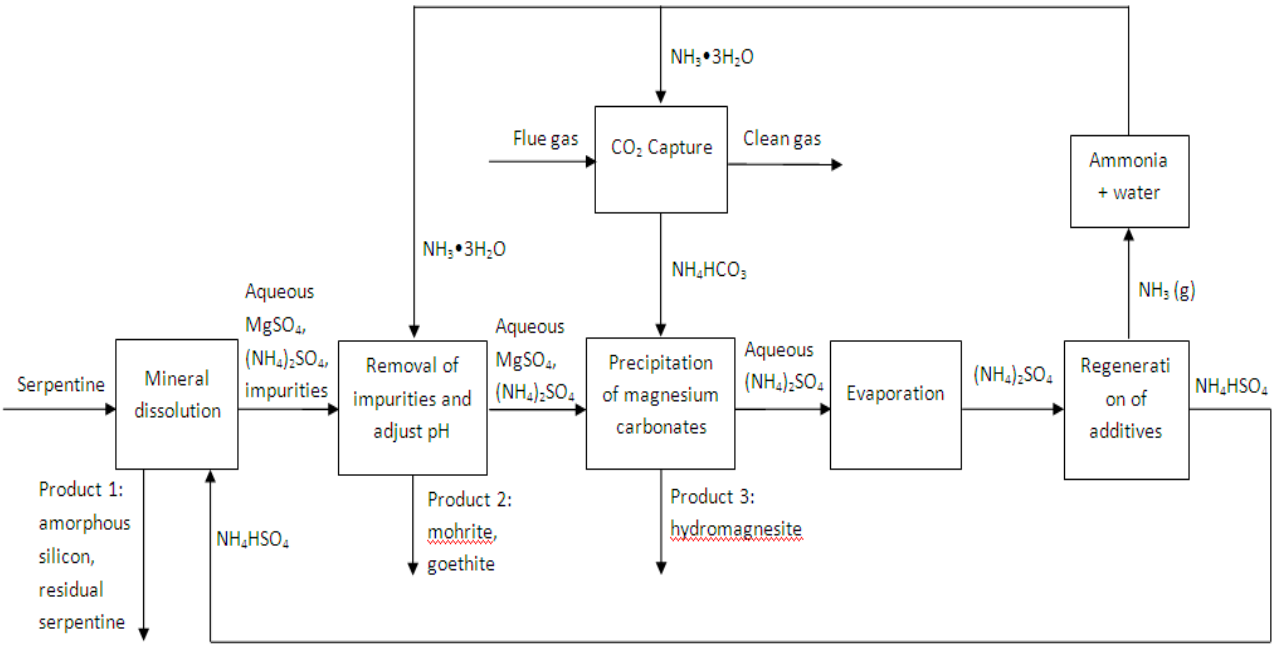

Figure 1: Schematic process route of pH-swing CO_2 mineral sequestration with recyclable ammonium salts.

Since the CO_2 capture with ammonia is a relatively mature technology, this paper focuses on the serpentine dissolution using NH_4HSO_4, carbonation using NH_4HCO_3 and regeneration of ammonium salts by thermal decomposition.

2. Experimental methods

During the dissolution experiment, 20 grams of serpentine was added into 400ml 1.4 M NH_4HSO_4 solution. The solution was heated in a glass reactor to 100°C using a thermocouple-controlled silicon oil bath. After 3 hours dissolution, the solution was cooled down to room temperature and filtered with a 0.7 μm Pall syringe filters. The solid residue was dried at 105° for overnight. The solution was sampled and acidified for analysis, the concentration of dissolved magnesium, iron and other elements were measured using ICP-AES.

During the pH regulation and removal of impurities, 35% Ammonia water was titrated into solution form dissolution until the pH value was neutral. When the pH because stable, extra amount of 35% ammonia water was added to remove impurities.

During carbonation experiments, the pH regulated solution was put in a 500ml 3 necks glass vessel and heated up to 60°C by a silicon oil bath. Before the pre-heat of solution, 35% ammonia water was added. When the temperature had stabilised at 60°C, NH_4HCO_3 was added. Then, the solution was heated to 85°C and 2ml liquid samples were sampled by needle syringe at interval time. The liquid samples were filtered by mini filter unit and acidified with HNO_3. The liquid samples were analyzed by ICP-AES to measure the

concentration change of magnesium during precipitation. After the solution was stabilised at 90°C, the solution was kept at 85°C for 30 mins to maximise the carbonation. After that, the solution was cooled down and filtered with 0.7 μm Pall syringe filters.

3. Results and discussion

3.1 Serpentine dissolution

Studies were conducted to select the solvent that can extract highest amount of magnesium from serpentine [3]. NH_4HSO_4 was found to be the best sorbent and its extraction is even better than sulphuric acid which was thought to be the best [4]. The reaction of serpentine dissolution using NH_4HSO_4 is formulated in eq. (1) as below:

$$Mg_3Si_2O_5 \bullet (OH)_4 + 6NH_4HSO_4 \rightarrow 3MgSO_4 + 2SiO_2 + 5H_2O + 3(NH_4)_2SO_4 \quad (1)$$

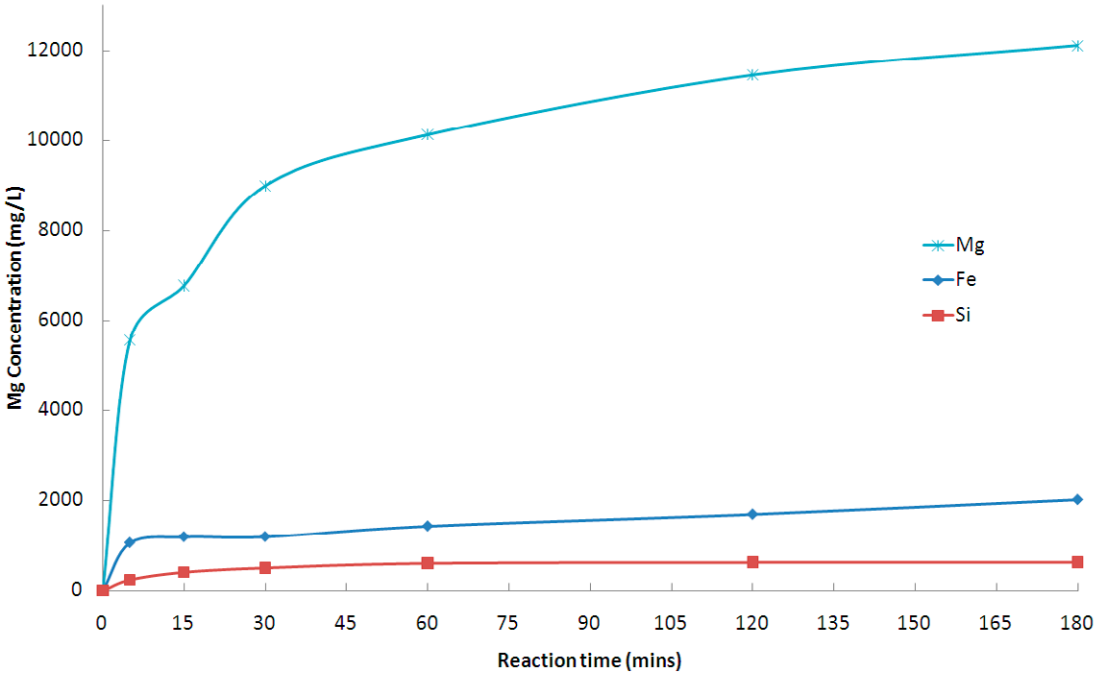

Figure 2: Mg, Fe and Si extraction efficiency variation with time at 100°C using NH_4HSO_4.

Figure 2 shows the results from extraction experiments. It can be seen that at 100 °C NH_4HSO_4 was able to extract 100% of magnesium from serpentine in 3 hours, 98% of iron, and only 17.6% of silicon. This incongruent leaching of Mg and Si could create a passive silicon layer on the surface of particle to block continue leaching of magnesium. In addition, it was found that the Mg extraction from serpentine increases with temperatures. The produced high Mg-rich leaching solution is suitable for precipitation of $MgCO_3$. The dissolution of kinetics were found to follow the model of constant size

particles, where the rate limiting mechanism of serpentine dissolution with NH_4HSO_4 is a chemical reaction with product layer diffusion control [3].

3.2 Precipitation of hydromagnesite from prepared Mg salts solution using NH_4HCO_3

After extraction with NH_4HSO_4, the Mg solution was acidic and ammonia water was added into the solution to raise the pH and remove impurities. The reactions of pH regulation and removal of impurities are listed below:

$$NH_4HSO_4 + NH_3 \bullet H_2O \rightarrow (NH_4)_2SO_4 + H_2O \quad (2)$$

$$(Fe, Al, Cr)_2(SO_4)_3 + 6NH_3 \bullet H_2O \rightarrow 2(Fe, Al, Cr)(OH)_3 \downarrow + 3(NH_4)_2SO_4 \quad (3)$$

$$(Zn, Cu, Mn)SO_4 + 2NH_3 \bullet H_2O \rightarrow (Zn, Cu, Mn)(OH)_2 \downarrow + (NH_4)_2SO_4 \quad (4)$$

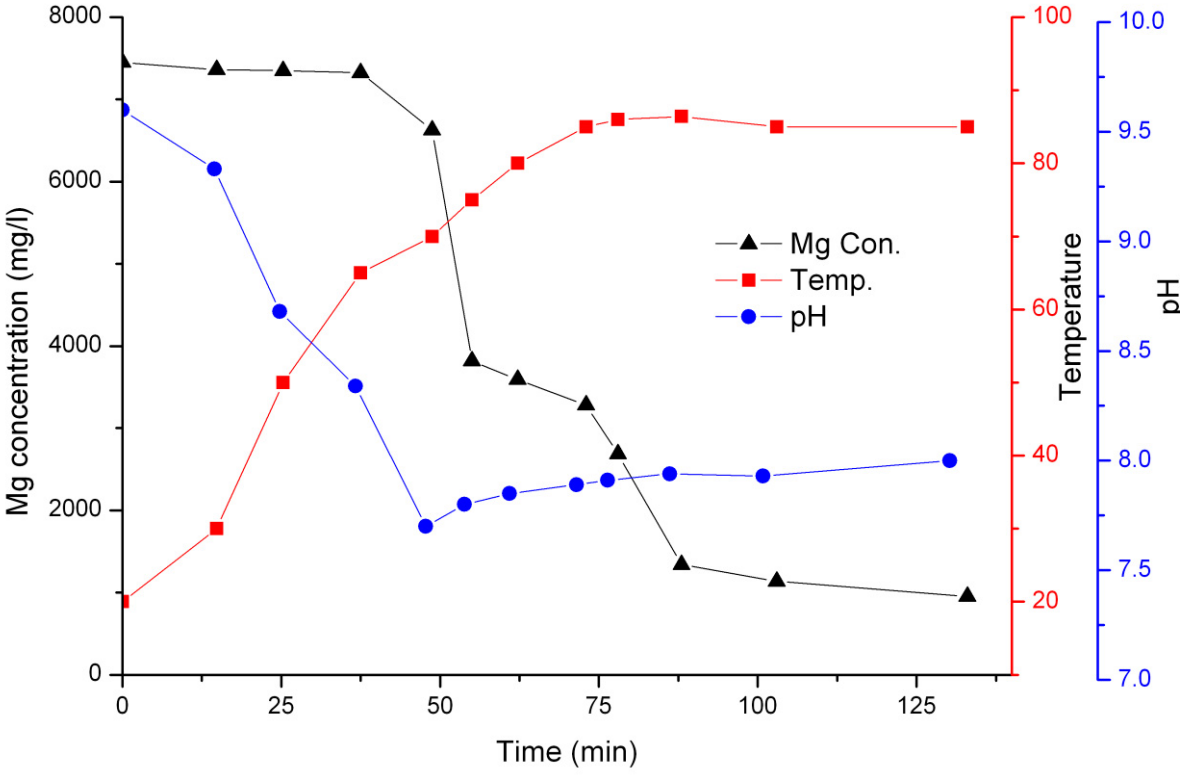

Figure 3: Temperature, time, pH and concentration of Mg in solution during the course of a typical carbonation experiment

The prepared Mg salts solution was then used for carbonation. Figure 3 shows the variation of temperature, time, pH and concentration of Mg in solution. Before the pre-heat of solution, 35% ammonia water was added. After the addition of ammonia water, the pH of solution decreased from 9.5 to 7.7 with the increasing of temperature. When the temperature had stabilised at 60°C, NH_4HCO_3 (as CO_2 source) was added. When NH_4HCO_3 was introduced, the pH increased a little bit to 8. No precipitation was formed in the initial stage. The concentration of magnesium started to drop when temperature went up to 70°C. In the following 5 mins, it was surprised to find that half of the Mg ions were precipitated at a very high rate. When the temperature was stabilised at 85°C, the pH became stable. Then, the solution was heated to 85°C and kept at 85°C for 30 mins to maximise the carbonation. The Mg was constantly precipitated and finally became steady. The actual precipitation reaction time took only around 30 mins, the reaction rate is much faster than the reported carbonation experiments of previous studies [5] [6] [7]. That high rate shows that the using of NH_4HCO_3 is more effective than using CO_2 for carbonates precipitation.

The precipitation reaction could be formulated in Eq. (5) as below:

$$5MgSO_4 + 5NH_4HCO_3 + 5NH_3 + 5H_2O \rightarrow 4MgCO_3 \bullet Mg(OH)_2 \bullet 5H_2O \downarrow + 5(NH_4)_2SO_4 \quad (5)$$

It has been found that the molar ratio of Mg-NH_4HCO_3-NH_3 (Mg indicates the Mg molar concentration in prepared solution from dissolution, NH_4HCO_3 indicates the amount added at 60°C, NH_3 indicates the amount added before pre-heat) is the key factor to carbonation efficiency, the highest carbonation efficiency 95.9% can be achieved.

4. Conclusions

An integrated CO_2 capture and storage based on mineral carbonation using recyclable ammonium salts was experimentally studied. Extraction of magnesium from serpentine was successfully performed using NH_4HSO_4 solution. The results from extraction experiments show that NH_4HSO_4 was able to extract 100% of magnesium from serpentine at 100 °C after 3 hours. In addition, it is found that the precipitation of hydromagnesite using NH_4HCO_3 solution is much more effective than using CO_2. The highest magnesium carbonation achieved 96% efficiency. Based on the experimental results, this process shows that the process has the potential to be cost-effective.

Acknowledgements

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